

WE CLAIM:

1. A selective hydrogenation catalyst consisting essentially of:
a precursor comprising at least one Group VIII metal disposed on an inorganic support;
a second metal selected from the group consisting of Group IB metals, Group IIB metals, Group IIIA metals, Group VIIB metals, and combinations thereof, disposed on the precursor;
wherein the catalyst is capable of selectively hydrogenating acetylene with a conversion S_c of at least about 95% and a selectivity to ethylene relative to ethane S_s of at least about 25 when the catalyst is employed in a steady-state liquid phase hydrogenation process.
2. The catalyst of claim 1 wherein the inorganic support comprises alumina.
3. The catalyst of claim 2 wherein the inorganic support comprises a particulate support.
4. The catalyst of claim 1 wherein the at least one Group VIII metal comprises palladium.
5. The catalyst of claim 4 wherein the second metal is selected from the group consisting of Group IIB metals, and combinations thereof.
6. The catalyst of claim 5 wherein the second metal comprises Zn.
7. The catalyst of claim 4 wherein the second metal is selected from the group consisting of Group IB metals, and combinations thereof.
8. The catalyst of claim 4 wherein the second metal is selected from the group consisting of Group VIIB metals, and combinations thereof.
9. The catalyst of claim 8 wherein the second metal comprises Mn.
10. The catalyst of claim 4 wherein the second metal is selected from the group consisting of Group IIIA metals, and combinations thereof.

11. The catalyst of claim 10 wherein the second metal is selected from the group consisting of In, Ga, and combinations thereof.
12. The catalyst of claim 4 wherein the second metal is selected from the group consisting of In, Ga, Mn, Zn, and combinations thereof.
13. The catalyst of claim 12 wherein the catalyst is capable of sustained activity for acetylene hydrogenation for at least about 150 hours.
14. A composition comprising:
 - a support;
 - a Group VIII metal disposed on the support;
 - a second metal selected from the group consisting of Group IIIA metals, Group IIB metals, Group VIIB metals, and combinations thereof, disposed on the support;
 - said composition characterized by substantially sustained activity for selective hydrogenation.
15. The composition of claim 14 wherein said sustained activity for selective hydrogenation comprises sustained activity for liquid-phase selective hydrogenation.
16. The composition of claim 15 wherein said selective hydrogenation comprises selective hydrogenation of acetylene.
17. The composition of claim 16 wherein the activity is sustainable for at least about 150 hours.
18. The composition of claim 16 further comprising a selectivity of ethylene relative to ethane S_s greater than or equal to about 25.
19. The composition of claim 18 further comprising an acetylene conversion S_c of about 95% or greater.

20. The composition of claim 16 wherein the second metal is selected from the group consisting of Mn, In, Ga, Zn, and combinations thereof.
21. The composition of claim 20 wherein the second metal comprises Mn.
22. The composition of claim 15 wherein the concentration of said Group VIII metal is within the range of from about 0.1 wt-% to about 1.0 wt-%.
23. The composition of claim 22 wherein the concentration of said Group VIII metal is within the range of from about 0.2 wt-% to about 0.8 wt-%.
24. The composition of claim 23 wherein the concentration of said Group VIII metal is within the range of from about 0.2 wt-% to about 0.5 wt-%.
25. The composition of claim 22 wherein the concentration of said second metal is within the range of from about 0.05 wt-% to about 2.0 wt-%.
26. The composition of claim 25 wherein the concentration of said second metal is within the range of from about 0.05 wt-% to about 1.2 wt-%.
27. The composition of claim 26 wherein the concentration of said second metal is within the range of from about 0.05 wt-% to about 1.0 wt-%.
28. The composition of claim 27 wherein the concentration of said second metal is within the range of from about 0.05 wt-% to about 0.5 wt-%.
29. The composition of claim 28 wherein the concentration of said second metal is within the range of from about 0.1 wt-% to about 0.5 wt-%.
30. The composition of claim 29 wherein the second metal is selected from the group consisting of Mn, In, Ga, Zn, and combinations thereof.

31. The composition of claim 30 wherein the second metal comprises Mn.
32. The composition of claim 29 wherein the Group VIII metal comprises Pd.
33. The composition of claim 32 wherein the second metal is selected from the group consisting of Mn, In, Ga, Zn, and combinations thereof.
34. The composition of claim 33 wherein the second metal comprises Mn.
35. The composition of claim 33 wherein the second metal comprises In or Ga.
36. The composition of claim 33 wherein the second metal comprises Zn.
37. A catalyst active for liquid-phase selective hydrogenation comprising:
Pd supported on particulate alumina;
a subsequently supported second metal selected from the group consisting of Ga, In, Mn, Zn, and combinations thereof;
a once-through acetylene conversion S_c of at least about 95%; and
a selectivity for ethylene relative to ethane S_s of at least about 40.
38. The catalyst of claim 37 further comprising a sustained activity for selective hydrogenation of at least 150 hours.
39. The catalyst of claim 38 wherein the second metal comprises from about 0.05 % to about 1 % of the catalyst by weight.
40. The catalyst of claim 39 wherein the Pd comprises from about 0.1 % to about 1.0 % of the catalyst by weight.
41. The catalyst of claim 40 wherein the Pd comprises from about 0.2 % to about 0.5 % of the catalyst by weight.

42. The catalyst of claim 39 wherein the second metal comprises from about 0.05 % to about 0.5 % of the catalyst by weight.
43. The catalyst of claim 42 wherein the Pd comprises from about 0.1 % to about 1.0 % of the catalyst by weight.
44. The catalyst of claim 43 wherein the Pd comprises from about 0.2 % to about 0.5 % of the catalyst by weight.
45. The catalyst of claim 44 wherein the second metal is Mn.
46. The catalyst of claim 44 wherein the second metal is In or Ga.
47. The catalyst of claim 44 wherein the second metal is Zn.
48. The catalyst of claim 38 wherein the second metal is Mn.
49. The catalyst of claim 38 wherein the second metal is In or Ga.
50. The catalyst of claim 38 wherein the second metal is Zn.
51. A supported catalyst for selective hydrogenation comprising:
a Group VIII metal;
a second metal selected from the group consisting of Group IB metals, Group IIB metals, Group IIIA metals, Group VIIB metals, and combinations thereof; and
a single-pass conversion S_c of at least 90% in liquid-phase hydrogenation of acetylene.
52. The catalyst of claim 51 wherein the second metal is selected from the group consisting of Group IIIA metals, Group IIB metals, Group VIIB metals, and combinations thereof.
53. The catalyst of claim 52 further comprising a selectivity for ethylene relative to ethane S_s of at least 40.

54. The catalyst of claim 53 wherein the second metal comprises about 0.05 wt-% to 1.0 wt-% of the catalyst by weight.
55. The catalyst of claim 54 wherein the second metal comprises about 0.1 wt-% to 0.5 wt-% of the catalyst by weight.
56. The catalyst of claim 55 further comprising a sustained activity for selective hydrogenation of acetylene of about 150 hours or greater.
57. The catalyst of claim 56 wherein the second metal is selected from the group consisting of Ga, Mn, In, Zn, and combinations thereof.
58. The catalyst of claim 57 wherein the Group VIII metal and the second metal are applied to the catalyst sequentially.
59. The catalyst of claim 58 wherein the second metal is applied to the catalyst after the Group VIII metal.
60. The catalyst of claim 57 wherein the second metal and the Group VIII metal are applied to the catalyst at about the same time.
61. The catalyst of claim 59 wherein the Group VIII metal is Pd.
62. The catalyst of claim 61 wherein the catalyst comprises an alumina support.
63. The catalyst of claim 62 wherein the support is a particulate support.
64. The catalyst of claim 63 wherein the particles have a minimum dimension between about 0.01 in. and about 0.2 in.
65. The catalyst of claim 64 wherein the particles have a minimum dimension between about 0.01 in. and about 0.02 in.

66. A supported catalyst for selective hydrogenation comprising:
a first metal selected from the group consisting of Group VIII metals and combinations thereof;
a second metal selected from the group consisting of Group IIIA metals, Group IIB metals, Group VIIB metals, and combinations thereof; and
an ethylene selectivity relative to ethane S_e of at least 20 in liquid-phase hydrogenation of acetylene.
67. The catalyst of claim 66 wherein the ratio of the amounts of the first metal to the second metal in the catalyst is from about 6 to about 0.25.
68. The catalyst of claim 67 wherein the ratio of the amounts of the first metal to the second metal in the catalyst is from about 3 to about 0.5.
69. The catalyst of claim 68 wherein the Group VIII metal is palladium.
70. The catalyst of claim 69 wherein the second metal is Zn.
71. The catalyst of claim 69 wherein the second metal is Mn.
72. The catalyst of claim 69 wherein the second metal is selected from the group consisting of Group IIIA metals and combinations thereof.
73. The catalyst of claim 72 wherein the second metal is selected from the group consisting of In, Ga, and combinations thereof.
74. The catalyst of claim 73 wherein the ethylene selectivity relative to ethane S_e is greater than 40.
75. The catalyst of claim 74 further comprising a sustained activity in selective hydrogenation of greater than 100 hours.

76. The catalyst of claim 75 further comprising an acetylene conversion S_c greater than or equal to 90%.
77. The catalyst of claim 76 further comprising an acetylene conversion S_c greater than 95%.
78. A method of screening catalysts for liquid-phase selective hydrogenation comprising:
preparing a test catalyst by adding a promoter selected from the group consisting of Group IB metals, Group IIB metals, Group IIIA metals, Group VIIB metals, and combinations thereof, to a reference catalyst comprising a supported Group VIII metal catalyst precursor;
preparing a liquid reactant stream comprising between 1 wt-% and 10 wt-% C_2H_2 dissolved in n-methyl-2-pyrrolidone;
testing the test catalyst and the reference catalyst by contacting the reactant stream and an approximately 2:1 $H_2:CO$ gas mixture in continuous flow with the test catalyst and reference catalyst, respectively, at a feed ratio of $H_2:C_2H_2$ of from about 1:1 to about 4:1 at selective hydrogenation reaction conditions to produce a product stream,
condensing substantially all of the n-methyl-2-pyrrolidone from the product stream;
measuring the concentrations of products comprising C_2H_2 , C_2H_4 , and C_2H_6 in the product stream at steady state;
determining performance parameters for the test catalyst and the reference catalyst comprising the respective C_2H_2 conversion S_c and C_2H_4 selectivity relative to C_2H_6 S_s ;
comparing the test catalyst performance parameters to those for the reference catalyst.
79. The method of claim 78 wherein said selective hydrogenation reaction conditions comprise a temperature in the range of about 100°C to about 150°C, and a pressure of from about 150 psig to about 250 psig.
80. The method of claim 79 further comprising diluting the test catalyst and reference catalyst with a catalyst surface area diluent.
81. The method of claim 80 wherein said catalyst surface area diluent comprises alumina.
82. The method of claim 81 wherein the catalyst support is a particulate support.

83. The method of claim 82 wherein testing is performed using a liquid phase reactant stream comprising from about 1.0 wt-% to about 5.0 wt-% C_2H_2 dissolved in n-methyl-2-pyrrolidone.
84. A method of making a promoted catalyst for selective hydrogenation comprising:
impregnating a carrier by incipient wetness impregnation with an aqueous solution of a promoter selected from the group consisting of Group IB metals, Group IIB metals, Group IIIA metals, Group VIIB metals, and combinations thereof, in a concentration sufficient to deposit the promoter on the carrier in a finished concentration of from about 0.05 wt-% to about 1.0 wt-%;
drying the product of the impregnation for about one hour at about 150°C;
calcining the dried product at about 300°C;
reducing the calcined product for 1 – 2 hours at a temperature in the range of from about 100°C to about 425°C in an atmosphere consisting of an approximately 2:1 mixture of $H_2:CO$ at a pressure of from about 150 psig to about 250 psig.
85. The method of claim 84 wherein the promoter is selected from the group consisting of Group IIIA metals, Group IIB metals, Group VIIB metals, and combinations thereof.
86. The method of claim 85 wherein the promoter is selected from the group consisting of In, Ga, Mn, Zn, and combinations thereof.
87. The method of claim 86 wherein the promoter is Mn or Zn.
88. The method of claim 87 wherein the carrier comprises a Group VIII metal disposed on a support.
89. The method of claim 88 wherein the support comprises particulate alumina.
90. The method of claim 89 wherein the finished concentration of the Group VIII metal is within the range of 0.1 wt-% to 10 wt-%.
91. The method of claim 90 wherein the Group VIII metal is Pd.

92. The method of claim 91 wherein the finished concentration of Pd is within the range of 0.2 wt-% to 0.8 wt-%.
93. The method of claim 92 wherein the finished concentration of Pd is from about 0.2 wt-% to about 0.5 wt-%.
94. The method of claim 92 wherein the promoter is selected from the group consisting of Group IIIA metals, Group IIB metals, Group VIIB metals, and combinations thereof.
95. The method of claim 94 wherein the promoter is selected from the group consisting of Mn, In, Ga, Zn, and combinations thereof.
96. The method of claim 95 wherein the promoter is Mn or Zn.
97. The method of claim 95 wherein the aqueous solution comprises an aqueous solution of the nitrate salt of the promoter, and the reduction is carried out at about 400-420°C for about one hour.
98. The method of claim 84 wherein the promoter is selected from the group consisting of Group IB metals and combinations thereof, the aqueous solution comprises an aqueous solution of a salt of the promoter, and the reduction is carried out at about 100°C for about two hours.
99. The method of claim 84 further comprising impregnating the carrier by incipient wetness impregnation with a solution comprising a metal selected from the group consisting of Group VIII metals and combinations thereof, in a concentration sufficient to deposit the metal on the carrier in a finished concentration of from about 0.1 wt-% to about 5.0 wt-%.
100. The method of claim 99 wherein the impregnation steps are performed simultaneously.
101. The method of claim 100 wherein the promoter is selected from the group consisting of Group IIIA metals, Group IIB metals, Group VIIB metals, and combinations thereof.

102. The method of claim 101 wherein the promoter is selected from the group consisting of In, Ga, Mn, Zn, and combinations thereof.
103. The method of claim 102 wherein the promoter is Mn or Zn.
104. The method of claim 102 wherein the carrier comprises alumina.
105. The method of claim 104 wherein the alumina comprises particulate alumina.
106. The method of claim 105 wherein the Group VIII metal is Pd.
107. The method of claim 106 wherein the finished concentration of Pd is from about 0.1 wt-% to about 1.0 wt-%.
108. The method of claim 107 wherein the promoter is selected from the group consisting of Mn, In, Ga, Zn, and combinations thereof.
109. The method of claim 108 wherein the promoter is Mn or Zn.
110. A catalyst made in accordance with the method of claim 95.
111. A catalyst made in accordance with the method of claim 109.
112. A hydrogenation catalyst made by a process comprising:
applying a first metal to a support;
applying a second metal to the support;
drying the first and second metal-coated support;
calcining the dried first and second metal-coated support to provide a precursor;
reducing the precursor;
wherein the first metal comprises a Group VIII metal and is applied to provide 0.1% - 1.0% by weight of the first metal to final weight of the catalyst;

wherein the second metal is selected from the group consisting of Group IIIA metals, Group IIB metals, Group VIIB metals, and combinations thereof, and applied to provide 0.05% - 1.2% by weight of the second metal to final weight of the catalyst;

wherein said first and second metals are applied such that the catalyst is capable of a sustained activity for selective hydrogenation of at least 150 hours and a once-through conversion S_c of at least 95% in liquid-phase hydrogenation of acetylene.

113. The process of claim 112 wherein the first and second metals are applied to the support concurrently.

114. The process of claim 112 wherein the second metal is selected from the group consisting of Group IIIA metals, Group IIB metals, Group VIIB metals, and combinations thereof, and applied to provide 0.1% - 0.5% by weight of second metal to final weight of the catalyst.

115. The process of claim 114 wherein the second metal is selected from the group consisting of Mn, In, Ga, Zn, and combinations thereof.

116. The process of claim 115 wherein the second metal comprises Mn or Zn.

117. The process of claim 115 wherein the first metal comprises Pd.

118. The process of claim 115 further comprising reducing the precursor for 1 – 2 hours at a temperature in the range of from about 100°C to about 425°C in an atmosphere consisting of an approximately 2:1 mixture of H₂:CO at about 250 psig.

119. The process of claim 115 wherein the selective hydrogenation reaction conditions comprise a temperature in the range of about 100°C to about 150°C, and a pressure of from about 150 psig to about 250 psig.